

# Dynamical Dzyaloshinsky-Moriya Interaction in $\text{KCuF}_3$

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The spin dynamics of the prototypical quasi one-dimensional antiferromagnetic Heisenberg spin  $S = 1/2$  chain  $\text{KCuF}_3$  is investigated by electron spin resonance spectroscopy. Our analysis shows that the peculiarities of the spin dynamics require a new *dynamical* form of the antisymmetric anisotropic spin-spin interaction. This dynamical Dzyaloshinsky-Moriya interaction is related to strong oscillations of the bridging fluorine ions perpendicular to the crystallographic  $c$  axis. This new mechanism allows to resolve consistently the controversies in observation of the magnetic and structural properties of this orbitally ordered perovskite compound.

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The perovskite system  $\text{KCuF}_3$  is presumably one of the best realizations of an one-dimensional (1D) antiferromagnetic (AFM) Heisenberg chain as a direct consequence of the orbital ordering in this compound [1]. Recently, detailed inelastic neutron scattering investigations have shown that fingerprints of a 1D Luttinger liquid, namely the spinon excitation continuum, exist up to temperatures of about 200 K [2]. Moreover, these specifically 1D features are still observable below the onset of antiferromagnetic ordering at  $T_N = 39$  K, indicating the strong quantum nature of magnetism in  $\text{KCuF}_3$ .

In spite of its paradigmatic status, the driving forces of the orbital and magnetic structure are far from being understood at the moment. Even the crystal structure originally assigned to be tetragonal  $D_{4h}^{18}$  (see Fig. 1) was claimed [3] to be orthorhombic  $D_2^4$ . Electron spin resonance (ESR) measurements [4, 5] played a key role in triggering these investigations: they suggested the existence of the antisymmetric anisotropic exchange, usually termed as Dzyaloshinsky-Moriya (DM) interaction, thereby questioning the crystal symmetry determined earlier. But the orthorhombic distortion deduced from x-ray diffraction [3] is not consistent with recent NQR data [6] and other experimental and theoretical findings [5, 7].

In this Letter we reanalyze all *static* sources of the ESR line broadening on the microscopical level and show that the discrepancies in the understanding of this paradigm compound can be resolved by introducing a *dynamical* Dzyaloshinsky-Moriya (dDM) interaction.

Single crystals of  $\text{KCuF}_3$  have been grown as described in Ref. 8. The ESR experiments were carried out with a Bruker ELEXSYS E500 CW-spectrometer at frequencies of 9 and 34 GHz. For measurements at 90 and 150 GHz a quasi-optical technique was used [9]. The ESR

spectrum consists of a single exchange narrowed Lorentz line at resonance fields corresponding to  $g_c = 2.15$  and  $g_a = 2.27$  in accordance with previous experiments at 24 GHz [10] and 34 GHz [11]. Figure 2 shows the temperature dependence of the ESR linewidth for different frequencies. Above  $T_N$  the linewidth increases monotonously from 0.3 kOe to more than 3 kOe above room temperature with a pronounced anisotropy with respect to the  $c$ -axis (see Fig. 2(b)), but without any anisotropy within the  $ab$  plane in agreement with the all over tetragonal crystal structure. For different frequencies the linewidth data follow approximately the same temperature dependence with comparable absolute values. It can be described phenomenologically by an Arrhenius law  $\Delta H \propto \exp(-\Delta/T)$  with an energy gap  $\Delta = 114$  K (see Fig. 2).

Using conventional estimates [12] for all relevant

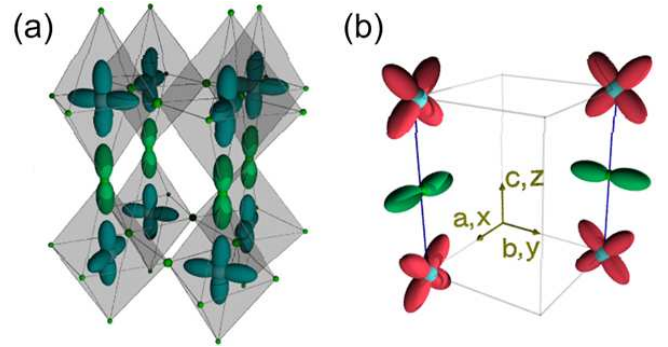


FIG. 1: (color online) (a): Schematic orbital ordering in the ground state of type- $a$   $\text{KCuF}_3$ . The big (small) spheres denote Cu (F) ions. The K ions, placed between the  $\text{CuF}_6$  octahedra, are not shown. (b): Two most relevant exchange paths of the ring-like SAE between the excited states of Cu ions.

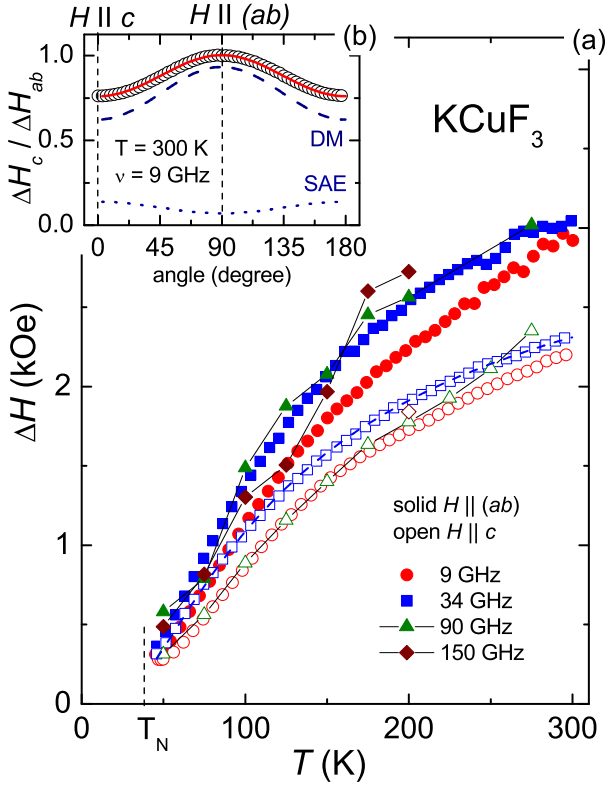


FIG. 2: (color online) (a) Temperature dependence of the linewidth at different frequencies. The blue dashed line (34 GHz,  $H||c$ ) represents a fit to an Arrhenius law. (b) Angular dependence of  $\Delta H$  at  $T = 300$  K. The fit is described in the text.

sources of the ESR linewidth, it was concluded that the relaxation contribution of the antisymmetric DM interaction is several orders of magnitude larger than all other mechanisms in  $\text{KCuF}_3$  [4]. However, the above mentioned inconsistencies concerning the direction of the DM vector [3, 4, 5] and a general theoretical analysis of the spin relaxation in  $S = 1/2$  chains [13, 14] questioned the validity of the original approach. Moreover, the microscopic analysis of the exchange paths in several one-dimensional magnets [15, 16, 17, 18] showed that the symmetric anisotropic exchange (SAE) may strongly exceed the conventional estimate and thus dominate the spin relaxation. Therefore, it is necessary to reanalyze microscopically the magnitude of SAE and DM interactions in  $\text{KCuF}_3$ .

Let us reconsider the structure and the orbital ordering in  $\text{KCuF}_3$ . The crystal has a pseudo-perovskite structure with  $a = 5.855$  Å,  $c = 7.852$  Å. Each  $\text{Cu}^{2+}$  ion (electronic configuration  $3d^9$ , spin  $S = 1/2$ ) is surrounded by a tetragonally deformed fluorine octahedron. The principal axes of the octahedra are oriented alternating along the  $a$  and  $b$  axes, leading to the orbital ordering of the ground  $|y^2 - z^2\rangle$  and  $|x^2 - z^2\rangle$  states of a hole on Cu ions (see Fig. 1(a)). The existing small contribution of the

$|3z^2 - r^2\rangle$  orbital to the ground state is not significant for the anisotropic exchange and will be neglected in the following analysis.

The crystal structure and the orbital ordering in  $\text{KCuF}_3$  allow for SAE interaction  $\mathcal{H}_{\text{SAE}}^{(ab)} = S_\alpha^a \cdot D_{\alpha\beta}^{(ab)} \cdot S_\beta^b$  ( $\{\alpha, \beta\} = \{x, y, z\}$ ,  $a, b$  are the interacting ions) only along the crystallographic  $c \equiv z$  axis via the ring-like processes described in Ref. 17. From the microscopical point of view, the exchange process consists of the excitation of a spin via spin-orbit (SO) coupling into an excited state of the starting ion  $a$ , the following hopping into an excited orbital state on the neighboring ion  $b$  and its transfer back into the initial state via the ground orbital state of the ion  $b$ . Fig. 1 shows that the overlap between the ground and the relevant excited orbital states ( $|xz\rangle$ ,  $|yz\rangle$ ) via  $\text{F}^- p$  orbitals is of  $\sigma$  and  $\pi$  type, respectively. Denoting the respective hopping integrals by  $t'_\sigma$  and  $t_\pi$ , we can estimate the exchange constant of SAE like in Ref. 17 as

$$D_{zz} \ll D_{xx} = D_{yy} \approx 4\lambda^2 \frac{t_\pi t'_\sigma}{\Delta_{cf}^2 \Delta_{ab}} \approx 1 \text{ K}, \quad (1)$$

where  $\lambda$  is the SO coupling constant,  $\Delta_{cf}$  and  $\Delta_{ab}$  denote the crystal-field splitting and the charge-transfer energy, respectively. Here we used  $\lambda_a/\Delta_{cf} = 0.05$  [15] and  $4t_\pi t'_\sigma/\Delta_{ab} \approx 4t_\sigma'^2/\Delta_{ab} \approx 380$  K [19].

The obtained value of SAE turns out to be strongly enhanced as compared to the conventional estimate [5, 19], but the resulting ESR line broadening with  $\Delta H \sim 10^2$  Oe cannot explain the huge ESR linewidth  $\Delta H \sim 3$  kOe observed in  $\text{KCuF}_3$ . Note that in all compounds where SAE plays a dominant role [15, 16, 17] the characteristic linewidth at  $T \approx J/k_B$  is about hundreds of Oe, i. e. an order of magnitude smaller than in the case of  $\text{KCuF}_3$ . This large discrepancy indicates the existence of an additional source of line broadening in  $\text{KCuF}_3$ . Indeed, Oshikawa and Affleck [13] supposed another type of spin relaxation to be dominant in this system, because  $\text{KCuF}_3$  does not obey the universal scaling behavior of  $\Delta H(T/J)$  typical for spin relaxation via SAE. Therefore, we will turn now to the analysis of the second possible source of the ESR line broadening in  $\text{KCuF}_3$  – the DM interaction:

The existence of a static DM interaction is not allowed in the originally proposed tetragonal crystal structure [4]. However, AFM resonance at  $T = 4.2$  K yields nonvanishing DM vectors  $\mathbf{d} \parallel [100]$  and  $[010]$  [5]. The reexamination of the room temperature crystal structure by x-ray diffraction [3] showed a large standard deviation of the fluorine ions placed on the magnetic chains away from the  $c$  axis. This was interpreted as a sign of a considerable *static* displacement of these ions from the  $c$  axis, leading to an orthorhombic distortion allowing for a non-vanishing DM vector directed along the  $[110]$  and equivalent directions. This kind of displacement in a perovskite structure usually means a rotation of a  $\text{CuF}_6$  octahedron

as a whole [20], but no displacement of the  $F^-$  ions from the  $(xy)$  plane has been detected in Ref. 3. This fact was emphasized by Binggeli *et al.* [7] who found in their LDA+U calculations that this structure relaxes to the conventional tetragonal structure of  $KCuF_3$ . This indicates that the displacements reported in Ref. 3 are rather *dynamic*, initiated by thermal fluctuations. This assumption is corroborated by the measurements of the thermal displacement coefficients of fluorine ions [21]. They were found to be very high and exceed strongly those of e. g. oxygen atoms in an oxide with the similar crystal structure  $LaMnO_3$  [22]. Such thermal motions may appear as static on the frequency scale of x-ray experiments  $f \sim 10^{15}$  Hz. In the following we develop a model of *dynamical anisotropic exchange*, which accounts for the thermal vibration of an intermediate diamagnetic ion and allows to explain both the magnitude and the anisotropy of the ESR line in  $KCuF_3$ .

We start from the general expression for the antisymmetric exchange interaction  $\mathcal{H}_{DM} = \mathbf{d}^{(ab)} \cdot [\mathbf{S}_a \times \mathbf{S}_b]$ . In the fifth order of perturbation we have derived

$$d_j^{(ab)} = \frac{2i}{\Delta_{\eta\xi}} \left( \frac{1}{\Delta_{\kappa\eta}\Delta_{\rho\eta}} + \frac{1}{\Delta_{\kappa\xi}\Delta_{\rho\xi}} \right) \left( t_{\xi\kappa}t_{\kappa\eta} \cdot \right. \quad (2)$$

$$\left. \frac{\langle \eta | \lambda_a l_j^{(a)} | \zeta \rangle}{\Delta_{\eta\zeta}} t_{\zeta\rho}t_{\rho\xi} - t_{\eta\rho}t_{\rho\xi} \frac{\langle \xi | \lambda_b l_j^{(b)} | \varphi \rangle}{\Delta_{\xi\varphi}} t_{\varphi\kappa}t_{\kappa\eta} \right),$$

where  $j = \{x, y, z\}$ ,  $t_{\alpha\beta}$  are the effective hopping integrals between the states  $|\alpha\rangle$ ,  $|\beta\rangle$  and a sum over all states of

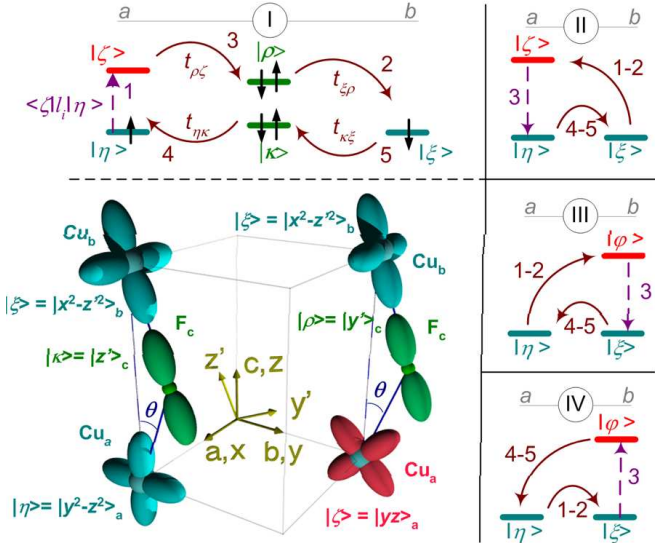


FIG. 3: (color online) Possible paths for DM interaction between two sites  $a$  (with ground state  $\eta$ , exited state  $\zeta$ ) and  $b$  ( $\xi$  and  $\varphi$ , respectively). Solid arrows correspond to the effective hopping integrals, dashed arrows indicate the matrix elements of the spin-orbit coupling. Numeration indicates one of the possible order of the matrix elements in Eq. (2). Frame (I) displays additionally orbital configurations corresponding to this exchange process.

an intermediate ion ( $|\kappa\rangle$ ,  $|\rho\rangle$ ) is implied. These virtual hopping processes are displayed schematically in Fig. 3, where e. g. frame (I) corresponds to the first term of Eq. (2). Note, that expression (2) differs strongly from the one suggested in Ref. 23, where the position of the bridging ion, crucial in our case, was not discussed.

It is well known [4, 23], that the static DM interaction is not allowed in the crystal structure of  $KCuF_3$  with the space group  $D_{4h}^{18}$ , but now we go beyond the static configuration. As illustrated in Fig. 3, the intermediate ion  $c$  may be temporarily shifted from its equilibrium position due to rotation or tilting phonon modes. If the average time of this displacement  $\tau_F \approx 2\pi/\omega_F$  is large compared to the characteristic time of electron exchange  $\tau_{ab} \approx \hbar/t_{ab}$ , several exchange processes shown in Fig. 3 can occur via the displaced ion giving rise to antisymmetric exchange. Usually  $t_{ab} \sim 0.5$  eV what allows to estimate  $\tau_{ab} \approx 10^{-2}\tau_F$  using the phonon frequency  $\omega_F/2\pi \sim 70$   $\text{cm}^{-1}$  as determined from Raman scattering experiments [24].

The relevant pattern of the  $F^-$  displacements away from the  $c$  axis is taken in accord to x-ray diffraction experiments [3]. It can be related to the orbital order in  $KCuF_3$  as follows: In Fig. 3 we show the geometry of exchange along with the ground state orbitals  $|\eta\rangle = |y^2 - z^2\rangle_a$  and  $|\xi\rangle = |x^2 - z^2\rangle_b$ . There are four short and two long Cu-F bonds in a  $CuF_6$  octahedron. A displacement of an intermediate  $F^-$  ion along the  $y_c$  axis (as shown in the Fig. 3) corresponds to the rotation of the  $Cu$   $|x^2 - z^2\rangle_b$  orbital and fluorine ion around the  $x_b$  axis and does not destroy short bonds. Note that in this case the  $|y^2 - z^2\rangle_a$  orbital is fixed by three stationary short bonds and is not rotated in accordance with the results of the structural analysis [3] which does not reveal any deviations of  $F^-$  ions from the  $(ab)$  plane. The second equivalent possibility, a displacement of the  $F^-$  ion along the  $x_c$  axis with the adiabatic rotation of the  $|y^2 - z^2\rangle_a$  around the  $y_a$  axis, is not displayed in the Fig. 3, but will be taken into account. Substituting the excited state  $|\varphi\rangle = |yz\rangle_a$  ( $\langle d_{yz} | l_x | d_{y^2-z^2} \rangle_a = 2i$ ), the Eq. (2) gives only one nonzero component of  $\mathbf{d}$

$$|d_x^{(ab)}| = 4 \frac{\lambda_a}{\Delta_{cf}} \frac{(2t'_\sigma + t_\pi)(t'_\sigma + t_\pi)t'_\sigma}{\Delta_{ab}\Delta_{ac}^2} \cdot [-t'_\sigma \cos^2(2\theta) + t_\pi \sin^2(2\theta)] \cos(2\theta) \sin(2\theta). \quad (3)$$

Note that the factor  $\sin(2\theta)$  can be rewritten as a modulus of the vector product  $[\mathbf{n}_{ac} \times \mathbf{n}_{bc}]$ , where the unit vectors  $\mathbf{n}_{ac}$  and  $\mathbf{n}_{bc}$  connect the spins  $a$  and  $b$  with the bridging ion  $c$ , respectively. Therefore, the rule  $\mathbf{d} \parallel [\mathbf{n}_{ac} \times \mathbf{n}_{bc}]$  suggested in Refs. 25, 26 for the static case is preserved in our case, too.

The value of  $\theta$  is related to the displacement of a  $F^-$  ion from equilibrium position  $\sin(2\theta) \cdot R_{Cu-F}$ , where  $R_{Cu-F}$  is the distance between the Cu and F ions and can be expressed via phonon operators. Thus we arrive to a new



dynamical form of DM interaction (dDM) containing simultaneously a phonon and two spin operators. A closely related form of spin-lattice interaction was introduced by Kochelaev [27] (see Eq. (5) in Ref. 28) in the context of explanation of the isotope effect on the ESR linewidth in lightly doped  $\text{La}_2\text{CuO}_4$ . In our case, however, we do not need to recall the conventional spin-phonon interaction (coupling parameter  $G$  in Refs. 27, 28) at all, which was a crucial ingredient in that approach.

In the following, we will use this dynamical Hamiltonian to calculate the ESR linewidth by the method of moments  $\Delta H \propto M_2(d^2)/J$  [12, 16, 18], where upon the thermal averaging over the phonon variables will be performed. Applying the Einstein model of vibration we get  $\langle \sin^2(2\theta) R_{\text{Cu-F}}^2 \rangle = \frac{2\hbar}{m\omega_F} \coth(\hbar\omega_F/2k_B T)$ , where  $m$  denotes the mass of an oscillating fluorine ion and  $\omega_F$  is the frequency of the rotating mode. The quantity  $\langle \sin(2\theta) R_{\text{Cu-F}} \rangle$  is naturally equal to zero and the static DM interaction does not exist. To compare with the results of x-ray analysis, it is useful to introduce the root-mean-square deviation of the  $\text{F}^-$  ion away from the  $c$  axis  $\Delta R_\perp = \sqrt{\langle \sin^2(2\theta) R_{\text{Cu-F}}^2 \rangle}$ . Using the typical rotation frequency of  $\text{CuF}_6$  octahedra  $\omega_F \sim 70 \text{ cm}^{-1}$  [24] one can estimate  $\Delta R_\perp \approx 0.07 \text{ \AA}$  at  $T = 100 \text{ K}$ , what coincides with Ref. 3. Therefore, we conclude that these displacements are rather dynamic than static at  $T > T_N$ . This conclusion is supported by the latest NQR study [6] which does not give any evidence for a static dislocation of  $\text{F}^-$  ions from the  $z$  axis at  $77 \text{ K}$  as well. To estimate  $d_x^{(ab)}$  we will use the values given in Eq. (3). Recalling the second possible direction of motion of intermediate  $\text{F}^-$  ions, we derive finally

$$|d_x^{(ab)}| = |d_y^{(ab)}| \approx 5.6 \text{ K}. \quad (4)$$

Note that this estimate coincides very well with the value  $d_{\text{AFM}}^{(ab)} \approx 5.13 \text{ K}$  employed by Yamada and Kato [5] to describe the anisotropy of the AFM resonance line below  $T_N$ . Moreover, it yields the correct linewidth of about  $10^3 \text{ Oe}$  in the high-temperature limit.

The anisotropic interchain exchange can be neglected, because of the small constant of isotropic exchange  $J_\perp \ll J$  and the orthogonality of orbital states. The dynamical form of SAE would arise in the higher order of perturbation theory as compared to the dDM interaction and is expected to be negligibly small. The anisotropic Zeeman effect does not contribute, because we do not observe any significant field dependence of the linewidth up to the frequency of  $150 \text{ GHz}$  (Fig. 2). Therefore, the spin relaxation mechanisms described above, the static SAE (Eq. 1) and the dDM interaction (Eq. 4) between the Cu ions along the  $c$  axis are the only relevant sources of the ESR line broadening in  $\text{KCuF}_3$ . Indeed, these two broadening mechanisms can explain both the magnitude and the anisotropy of the ESR linewidth. Figure 2(b) shows a fit of the angular dependence of  $\Delta H$  at room tempera-

ture and emphasizes the contributions of SAE and dDM interaction to the linewidth, which reflects clearly the dominant role of the dDM interaction. This indicates that  $\text{KCuF}_3$ , despite its paradigmatic status for orbital order, is governed by strong fluctuations in the lattice and orbital sector.

In summary, we have introduced a dynamical Dzyaloshinsky-Moriya (dDM) interaction which allowed to explain the long standing mystery about the origin of the huge ESR linewidth in  $\text{KCuF}_3$  at  $T > T_N$  in consistency with other experimental findings about the properties of this quasi-1D system. Such a dDM interaction becomes effective, if the characteristic time of the dynamic distortion resulting in a nonzero DM vector is large compared to the time scale of the exchange interaction and if the amplitude of these distortions is high. This is the case for low-lying optical modes with the tendency to soften to low temperatures. Therefore, such kind of interaction may be on general useful for understanding the spin dynamics of other materials with soft-mode vibrations.

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